



$(n\text{Bu}_4\text{N})_4\text{W}_{10}\text{O}_{32}$ -catalyzed selective oxygenation of cyclohexane by molecular oxygen under visible light irradiation

Wenfeng Wu, Zaihui Fu*, Senbei Tang, Shuai Zou, Xu Wen, Yue Meng, Shubin Sun, Jie Deng, Yachun Liu, Dulin Yin

National & Local United Engineering Laboratory for New Petrochemical Materials & Fine Utilization of Resources, Key Laboratory of Resource Fine-Processing and Advanced Materials of Hunan Province and Key Laboratory of Chemical Biology and Traditional Chinese Medicine Research (Ministry of Education of China), College of Chemistry and Chemical Engineering, Hunan Normal University, Changsha 410081, China

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ABSTRACT

The development of mild and efficient process for the selective oxygenation of organic compounds by molecular oxygen (O_2) can be one of the key technologies for synthesizing oxygenates. Here, the photo-oxygenation of cyclohexane to cyclohexanol and cyclohexanone over tetrabutylammonium decatungstate ($\text{W}_{10}\text{O}_{32}^{4-}$) was carried out under visible light irradiation and pure O_2 atmosphere. The $\text{W}_{10}\text{O}_{32}^{4-}$ was found to be active to this photo-oxygenation in a pure acetonitrile (MeCN), which can achieve ca. 8.1% cyclohexane conversion with ca. 64.3% selectivity for cyclohexanone under sustained visible light irradiation of 12 h. Notably, the above-described photo-catalysis oxygenation was improved to some extent in the presence of some acidic additives such as 10 M HCl, H_2SO_4 , or H_3PO_4 aqueous solution and benzenesulfonic acid, providing ca. 12.4–14.3% cyclohexane conversion with ca. 59.7–69.4% cyclohexanone selectivity. Moreover, this acid-promoted effect was further magnified in the case of adding a suitable amount of water, which can lead to enhancing conversion (16.8–20.0%) and improving cyclohexanone selectivity (68.2–78.3%). This acidic aqueous solution-promoted effect was also observed upon the $\text{W}_{10}\text{O}_{32}^{4-}$ -photocatalyzed oxygenation of other substrates like toluene, ethylbenzene and butanone. This is likely due to the acidic aqueous solutions playing important roles in improving photo-redox cycling of $\text{W}_{10}\text{O}_{32}^{4-}$ and preserving its stability, as supported by the UV-vis spectra and cyclic voltammetry measurements.

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1. Introduction

There is considerable interest in the search for efficient catalysis system that induces oxidation of inactivated C–H bonds by molecular oxygen under mild conditions. The oxidation of cyclohexane to cyclohexanone and cyclohexanol (as KA-oil), intermediate products in the synthesis of synthetic fibbers and fine chemicals [1,2], is an example of this transformation. The reaction remains in the center of interest of many research groups [2–4] as it is one of the least efficient of all major industrial chemical processes. In industrial process, large-scale oxygenation of cyclohexane to KA-oil, employs soluble cobalt or manganese salts as homogeneous catalysts under relatively harsh conditions (443–503 K and 10–20 atm of air) and produces KA-oil with 75–80% selectivity, cyclohexane conversion is usually limited to lower than 10% in order to prevent over-oxidation of the target products [3–6]. Some efficient catalysis processes

have been developed for selective oxygenation of cyclohexane by molecular oxygen [7–16]. However, most of these direct oxidation processes by molecular oxygen under heating generally need to employ harsh operating conditions because the triplet nature of molecular oxygen hampers the reaction with organic compounds in its singlet state, which rarely leads to the chemistry.

During recent years, photo-catalytic oxygenation has received enormous attention because of its potential application in environmental treatment [17–19] and the synthesis of fine chemicals [20,21]. On the other hand, the use of solar light and molecular oxygen as reagents in catalysis oxidations contributes to realizing innovative and economically advantageous processes for transformation of hydrocarbons into oxygenated products and, at the same time, to move toward a sustainable chemistry that has a minimal environmental impact. Up to now, some efficient photo-catalysts, such as TiO_2 [22–24], Fe– TiO_2 [25] and double-shelled WO_3/TiO_2 [26], Fenton reagent-assisted WO_3 [27], Cr– SiO_2 [28], $\text{V}_2\text{O}_5\text{--Al}_2\text{O}_3$ [29], NaY zeolite [30–32], trans-dioxoosmium(VI) complex [33], iron(III) porphyrin complexes [34,35], iron(III) chloride [36–38], copper(II) chloride [39,40] and decatungstate [41–49] have been

* Corresponding author. Tel.: +86 731 88872576; fax: +86 731 88872531.
E-mail address: fzhnnu@126.com (Z. Fu).

successfully applied to the field of UV or visible light-driven aerobic oxygenation or degradation of organic compounds. Among them, the decatungstate has been especially studied for its very important photo-catalytic properties and important advances have been achieved in the transformation of organic compounds to the corresponding oxidative products catalyzed by the decatungstate under UV light [47,48,50–54]. However, based on the facts that most of the solid catalysts commonly show a low photo-catalysis efficiency, the Fe porphyrin and especially Os complexes as efficient photo-catalysts are expensive, the efficient photo-catalysis system originating from a very cheap catalyst iron(III) or copper(II) chloride inevitably goes with considerable amounts of chlorination and the photo-catalysis activity of decatungstate is largely dependent on UV light irradiation. To the best of our knowledge, the decatungstate-catalyzed oxidation reactions under visible light has not been reported so far and how to mediate the photo-catalytic performance of decatungstate is hardly concerned. Herein, we report initial results obtained from using the visible light-driven decatungstate to catalyze aerobic oxidation of cyclohexane to KA oil in the presence of some acidic additives under pure O₂ atmosphere.

2. Experimental

2.1. Materials and apparatus

Materials and reagents used in this study were cyclohexane, benzene, toluene, ethylbenzene, butanone *n*-hexanol, acetonitrile (CH₃CN), sodium tungstate (Na₂WO₄), tetrabutylammonium bromide ([C₄H₉)₄N]₄Br), concentrated HCl, H₂SO₄, and H₃PO₄, acetic acid (HAc), benzenesulfonic acid, all of which were of analytical grade. Distilled water was used throughout this experiment.

2.1.1. UV-vis and IR spectra

Liquid UV-vis spectra of the sample in MeCN were recorded from 200 to 500 nm on UV-2450 spectrophotometer (Shimadzu, Japan). And transmission FT-IR spectrum of the sample was recorded from 400 to 4000 cm⁻¹ on a Nicolet Nexus 510 P FT-IR spectroscopy using a KBr disk.

2.1.2. CHN and W elemental analyses

CHN contents of the sample were measured on a Vario ELIII Elemental Analyzer (Germany) and its W content measured by a Perkin Elmer Optima 5300DV-ICP.

2.1.3. Cyclic voltammetric measurement

In cyclic voltammetric (CV) experiments, three-electrode configuration and an autolab electrochemical workstation (Eco Chemie, Holland) were used. A glassy carbon electrode (GCE, 3-mm diameter disk), sheet of platinum foil and KCl-saturated calomel electrode (SCE) were used as the working electrode (WE), counter electrode was and reference electrode, respectively. All the electrochemical experiments were carried out at room temperature (20 °C). All potentials here are reported *versus* the SCE.

2.2. Preparation of tetrabutylammonium decatungstate

Referring to published works [50,51], the preparation of tetrabutylammonium decatungstate ((C₄H₉)₄N₄W₁₀O₃₂, W₁₀O₃₂⁴⁻) is described as follows: 6.4 g (19.4 mmol) Na₂WO₄·2H₂O was dissolved with 40 mL of water in a three-necked flask (200 mL), followed by the addition of 13.4 mL of 3 M HCl aqueous solution. After the mixture was heated to boiling for 5–10 min, an aqueous solution of tetrabutylammonium bromide (1.3 M, 6 mL) was added to the mixture at 100 °C under continuous stirring and the white solid precipitated from the reaction solution. After cooling, the precipitate was filtered, washed with water (40 mL × 3 mL), and then

dried at 60 °C under vacuum to yield 5.5 g of W₁₀O₃₂⁴⁻. The measured CHN and W contents (theoretical value)/wt% for W₁₀O₃₂⁴⁻ were as follows: C, 22.35 (23.15), H, 4.23 (4.34), N, 1.49 (1.69), W, 54.89 (55.41). IR data for W₁₀O₃₂⁴⁻: 996, 972, 904, 800, 580, 435 and 400 cm⁻¹.

2.3. Procedure of photo-catalytic oxygenation

The visible light-driven oxygenation of cyclohexane by O₂ was performed in a self-assembly photo-reactor equipped with a water-cooled condenser (see our published work [40]), and a 35 W tungsten-bromine lamp equipped with a UV light filter (Osram brand) was immersed in the acetonitrile solution containing cyclohexane (1 mmol) and W₁₀O₃₂⁴⁻ (0.014 mmol). The reaction mixture was stirred magnetically under pure dioxygen atmosphere (1 atm) and sustained visible light irradiation, and the temperature of reaction solution increased to 36–38 °C because of the heating effect of light irradiation. After the desired irradiation time had elapsed, a small portion of reaction mixture (0.5 mL) was sampled from the reactor, and the products were quantitatively analyzed on an Agilent 6890N gas chromatograph (GC) with a DB-17 polysiloxane capillary column (30 m × 0.32 mm × 0.50 μm) and flame ionization detector (FID) using *n*-hexanol as an internal standard. Both the injector and detector temperature were 250 °C, and the column temperature was 100 °C. The isolated products were satisfactorily identified by comparing the MS spectra with those of the authentic samples. In addition, with triphenylphosphine to treat the filtrate for 1 h hardly changed selectivity of the products cyclohexanol and cyclohexanone, which showed the absence of cyclohexyl hydroperoxide in the products [55]. Each experiment was repeated in duplicate, the data deviation between two parallel experiments was lower than *ca.* 5%.

3. Results and discussion

3.1. Photo-catalytic performance of W₁₀O₃₂⁴⁻

Table 1 lists data for the W₁₀O₃₂⁴⁻-catalyzed oxygenation of cyclohexane with O₂ at 36–38 °C in MeCN containing various acidic additives under visible light irradiation. Entry 1 illustrates that the W₁₀O₃₂⁴⁻ was active to this photo-oxygenation, which could achieve *ca.* 8.1% cyclohexane conversion (turnover frequency (TOF), 0.48) in a pure CH₃CN medium under 12 h of sustained visible light irradiation, and afford cyclohexanol (selectivity (Sel.) 35.7%) and cyclohexanone (Sel. 64.3%) as its oxygenated products. However, if this catalytic oxygenation was carried out under heating, no any oxygenated products were observed at 38 °C for 12 h (see entry 2). This indicates that the present catalysis reaction is indeed triggered by visible light irradiation. Entry 3 shows that the photo-catalytic oxygenation was slightly improved in the presence of water, providing *ca.* 0.61 TOF with a similar product distribution to the entry 1. Entries 4–7 show that when a strong or medium acid, such as HCl, H₂SO₄, H₃PO₄ aqueous solution (10 M) or benzenesulfonic acid (PhSO₃H), was introduced into this photo-catalysis reaction system, the photo-catalysis efficiency was improved to some extent. Among these acidic additives, PhSO₃H achieved the highest TOF (0.85, entry 7) and H₃PO₄ provided the best selectivity for cyclohexanone (69.7%, entry 6). However, the addition of a weak acetic acid (HAc) to the photo-catalysis system contrarily resulted in a slight decrease in TOF (0.37, entry 8). Notably, when a suitable amount of water was introduced into the above acids-mediated photo-catalysis systems, the TOFs and cyclohexanone selectivity were further improved to some extent (entries 9–13). Among these photo-catalysis systems co-mediated by the additives acid and water, the highest TOF (1.19) was achieved in the co-presence of

Table 1Visible light-driven oxygenation of cyclohexane with molecular oxygen catalyzed by $W_{10}O_{32}^{4-}$ in the presence of various acidic solution additives.^a

Entry	Acid (mmol)	Water/mL	MeCN/mL	Conv. ^b /mol%	TOF ^c /h ⁻¹	Selectivity of products ^d (%)	
						Cyclohexanol	Cyclohexanone
1	–	–	5.5	8.1	0.48	35.7	64.3
2 ^e	–	–	5.5	0	0	0	0
3	–	0.5	5.0	10.2	0.61	36.0	64.0
4 ^f	HCl (1.0)	–	5.4	12.4	0.74	40.3	59.7
5 ^g	H ₂ SO ₄ (1.0)	–	5.4	13.5	0.80	39.9	60.1
6 ^h	H ₃ PO ₄ (1.0)	–	5.4	13.8	0.82	30.3	69.7
7 ⁱ	PhSO ₃ H (1.0)	–	5.5	14.3	0.85	35.8	64.2
8 ^j	HAc (1.0)	–	5.5	6.2	0.37	35.9	64.1
9 ^f	HCl (1.0)	0.5	4.9	20.0	1.19	31.8	68.2
10 ^g	H ₂ SO ₄ (1.0)	0.5	4.9	17.3	1.03	29.0	71.0
11 ^h	H ₃ PO ₄ (1.0)	0.5	4.9	16.8	1.00	28.4	71.6
12 ⁱ	PhSO ₃ H (1.0)	0.5	5.0	18.5	1.10	21.7	78.3
13 ^j	HAc (1.0)	0.5	5.0	8.0	0.48	45.9	54.1
14 ^k	–	–	5.5	5.9	0.35	37.9	62.1
15 ^{k,f}	HCl (1.0)	0.5	4.9	13.8	0.82	31.5	68.5

^a Cyclohexane (1.0 mmol), $W_{10}O_{32}^{4-}$ (0.014 mmol), O₂ (1 atm), temperature (36–38 °C), time (12 h), using 35 W of tungsten–bromine lamp as visible light source.^b Cyclohexane conversion = (\sum content (mmol) of each product measured via GC analysis/adding cyclohexane amount (mmol)) \times 100%.^c Turnover frequency based on cyclohexane.^d Product selectivity = the content of this product/ \sum content (mmol) of each product \times 100%.^e Under heating (38 °C).^f Adding 10 M HCl (0.1 mL).^g Adding 10 M H₂SO₄ (0.1 mL).^h Adding 10 M H₃PO₄ (0.1 mL).ⁱ Adding 1.0 mmol benzenesulfonic acid.^j Adding 1.0 mmol acetic acid.^k Using acetone as a solvent.

10 M HCl and water and the best selectivity for cyclohexanone (78.3%) obtained in the co-existence of PhSO₃H and water. Entries 14–15 illustrate that the present photo-catalysis oxygenation also proceeded in acetone and was promoted significantly by the co-additives 10 M HCl and H₂O, but provided lower TOFs (0.35 and 0.82) than those (0.48 and 1.19) in MeCN medium, being likely due to the poor solubility of $W_{10}O_{32}^{4-}$ in acetone.

3.1.1. Effect of various parameters

In the following experiments, the effect of catalyst concentration, HCl and water amounts, as well as irradiation time on the $W_{10}O_{32}^{4-}$ -photocatalyzed cyclohexane oxidation by O₂ in MeCN solvent was checked in the co-existence of 10 M HCl and water. Fig. 1 illustrates that when the concentration of catalyst was between 0.14 and 1.4 mol%, cyclohexane conversion linearly increased from 5.5 to 20.0% with the concentration, after that, the improved effect of catalyst concentration on this photo-oxidation was nearly neglected, being likely due to the decrease

in the catalyst's solubility in CH₃CN. Cyclohexanone selectivity continuously and slowly increased from 57.2 to 68.9% with the concentration. Fig. 2 shows that when the amount of HCl was enhanced from 0.125 to 1.0 mmol, cyclohexane conversion continuously and slowly ascended from 16.9 to 20.0%, with a concomitant increase in cyclohexanone selectivity from 52.3 to 68.2%. After that, the conversion and selectivity hardly increased with the further increasing HCl amount to 1.5 mmol. Fig. 3 presents that when the amount of water was between 0.1 and 0.5 mL, cyclohexane conversion and cyclohexanone selectivity continuously and slowly increased from 12.4 to 20.0% and from 50.7 to 68.2% with the amount, respectively. However, an attempt to further increase the amount of water from 0.5 to 1.5 mL contrarily resulted in the significantly decreased conversion and selectivity, this is likely because an excess amount of water can lead to the decreased solubility of substrate and catalyst in CH₃CN. Fig. 4 illustrates that when the time was prolonged from 6 to 32 h, the conversion continuously and significantly increased from 11.8 to 30.2%. After that, it hardly increased with the further prolonging

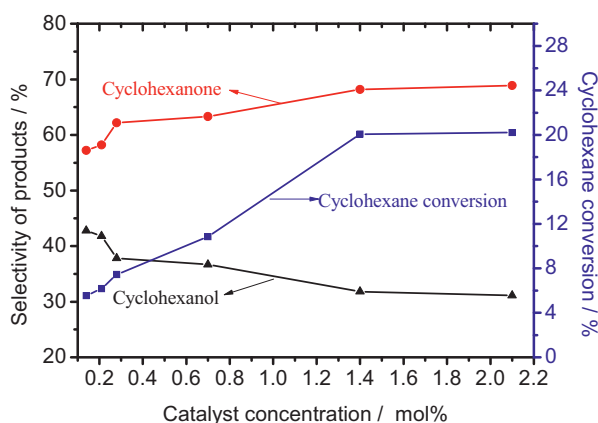


Fig. 1. Effect of the concentration of $W_{10}O_{32}^{4-}$ on the oxygenation of cyclohexane (1 mmol) by O₂ in MeCN (4.9 mL), HCl (10 M, 0.1 mL) and water (0.5 mL) under visible light irradiation (12 h).

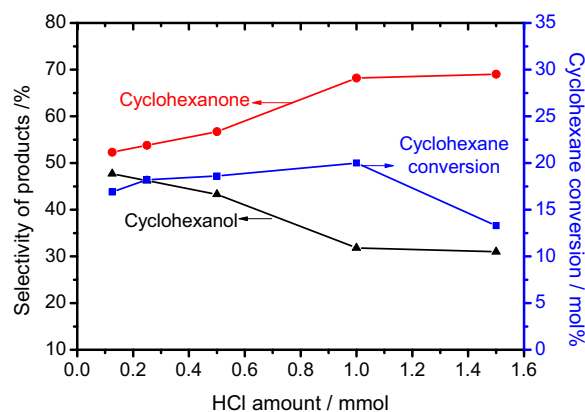


Fig. 2. Effect of HCl amount on the $W_{10}O_{32}^{4-}$ (0.014 mmol)-photocatalyzed cyclohexane (1 mmol) oxygenation by O₂ in MeCN (5.0 mL) and water (0.5 mL) under visible light irradiation (12 h).

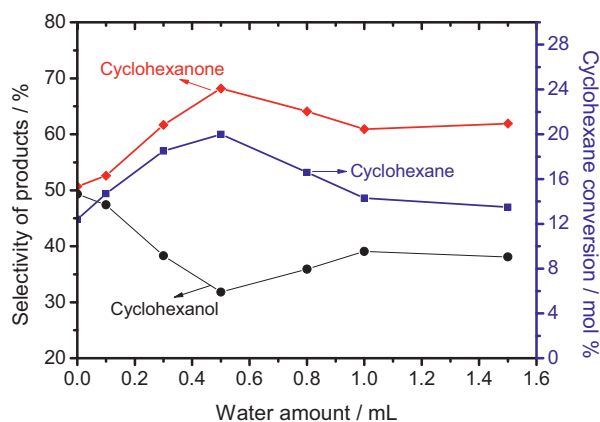


Fig. 3. Effect of water amount on the $W_{10}O_{32}^{4-}$ (0.014 mmol)-photocatalyzed cyclohexane (1 mmol) oxygenation in MeCN and HCl (10 M, 0.1 mL) under visible light (irradiation time, 12 h).

time to 36 h. On the whole, the selectivity for cyclohexanone slightly increased with the time, but its amplitude was lower than 4.0%. Fig. 5 compares the irradiation time-dependence of cyclohexane conversion for the present photo-catalysis oxygenation in the absence or presence of HCl aqueous solution. In the range of the examined irradiation time (6–36 h), the curve of conversion in a

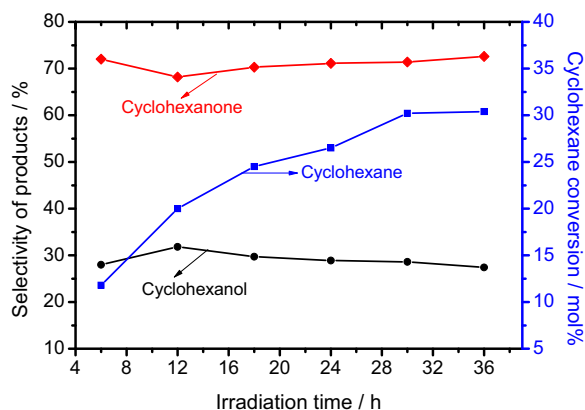


Fig. 4. Effect of irradiation time on the $W_{10}O_{32}^{4-}$ (0.014 mmol)-photocatalyzed oxygenation of cyclohexane (1 mmol) by O_2 in MeCN (4.9 mL) with HCl (10 M, 0.1 mL) and H_2O (0.5 mL).

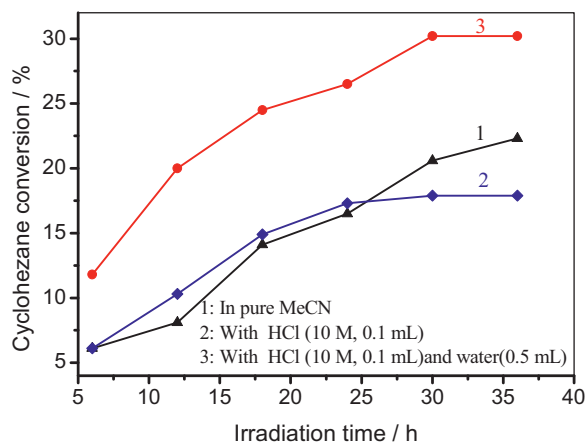


Fig. 5. A comparison of the effect of irradiation time on the conversion for the $W_{10}O_{32}^{4-}$ (0.014 mmol)-photocatalyzed oxygenation of cyclohexane (1 mmol) by O_2 in the absence and presence of HCl aqueous solution.

pure MeCN medium continuously climbed from 6.1 to 22.3% with the time (see curve 1 in Fig. 5). When the additive 10 M HCl solution was introduced into the photoreaction system, an increase in cyclohexane conversion with the time was only sustained to 24 h (curve 2, finally achieving ca. 17.3% conversion). If the additives 10 M HCl and water were simultaneously introduced into the photoreaction system, an increasing trend of the conversion with the time was prolonged to 32 h (curve 3). This likely implies that the photocatalyst $W_{10}O_{32}^{4-}$ is stable in a pure MeCN, and its stability becomes bad in the presence of only 10 M HCl, but can be effectively preserved in the co-existence of 10 M HCl and water.

Finally, the oxygenation of other substrates like benzene, toluene, ethylbenzene and butanone by O_2 in MeCN under visible light was examined using $W_{10}O_{32}^{4-}$ as a catalyst and the results are summarized in Table 2. Entries 1 and 2 show that $W_{10}O_{32}^{4-}$ was inactive to the photo-oxygenation of benzene by O_2 whether the additives 10 M HCl and water were present or not, demonstrating that the photo-excited $W_{10}O_{32}^{4-}$ is not capable of oxidizing the C–H bond in aromatic ring. Entries 3, 5 and 7 illustrate that $W_{10}O_{32}^{4-}$ was active for the side chain C–H bond oxygenation of toluene and ethylbenzene, as well as the α -C–H bond oxygenation of butanone under visible light, respectively providing benzaldehyde (yield, 2.9%) for toluene, acetophenone (4.7%) and α -phenethylalcohol (1.4%) for ethylbenzene, acetic acid (2.7%) and butanedione (1.9%) for butanone as their main oxygenation products. The photo-reactivity of various substrates over $W_{10}O_{32}^{4-}$ followed an increasing sequence of ethylbenzene > butanone > toluene. In comparison with the above-described reactions in a pure MeCN medium, these photo-oxygenations catalyzed by $W_{10}O_{32}^{4-}$ were also improved to some extent in the presence of 10 M HCl and water, which could lead to an increase in the conversion of substrates and the yield of goal oxygenated products (entries 4, 6 and 8). For example, ethylbenzene conversion and acetophenone yield were ca. 12.3 and 9.9% in the co-existence of 10 M HCl and water, being 1.00- and 1.06-fold higher than those obtained in a pure MeCN, respectively (entries 6 versus 5). This indicates that the promoted effect of acidic aqueous solution on the activity of $W_{10}O_{32}^{4-}$ commonly exists in the photo-catalyzed oxygenation of other substrates by O_2 under visible light.

3.2. Mediated mechanism of acidic aqueous solution

In order to explore the reason that acidic aqueous solution is capable of promoting the $W_{10}O_{32}^{4-}$ -photocatalyzed cyclohexane oxygenation by O_2 in MeCN under visible light irradiation, we measured the UV–vis absorption spectra of $W_{10}O_{32}^{4-}$ in the present photoreaction media and the result is shown in Fig. 6. The UV–vis spectrum of $W_{10}O_{32}^{4-}$ in a pure MeCN exhibited two characteristic adsorption bands in the 250–350 nm regions, in agreement with previous works [52,53]. The band at $\lambda = 320$ nm may be assigned to oxygen-to tungsten charge transition of four linear W–O–W bridge bonds in the $W_{10}O_{32}^{4-}$ structure [54] and another weak band at $\lambda = 262$ nm likely originates oxygen-to tungsten charge transition of the unstable structural subunit $[W_5O_{16}]^{2-}$ [56] or the kegglin structural $[H_2W_{12}O_{40}]^{6-}$ [57]. The additives water, or 10 M HCl and water resulted in an obvious decrease in the adsorption band at $\lambda = 262$ nm (see curves 2 and 4), likely indicating that water can effectively restrain the transformation of $W_{10}O_{32}^{4-}$ toward the $[W_5O_{16}]^{2-}$ or $[H_2W_{12}O_{40}]^{6-}$, as previously reported by some literature [58,59]. Notably, the additive 10 M HCl resulted in a blue shift of the adsorption band at $\lambda = 320$ nm and the absorbance at $\lambda = 262$ nm being weakened into a shoulder (see curve 3). The inset in Fig. 6 further shows that the absorbance of $W_{10}O_{32}^{4-}$ in the visible region of 400–500 nm was hardly influenced by the additives water, or water and 10 M HCl, but slightly decreased in the presence of only 10 M HCl. After these systems above-described

Table 2Visible light-driven oxygenation of other substrates with molecular oxygen catalyzed by $W_{10}O_{32}^{4-}$ in the absence and presence of 10 M HCl and water.^a

Entry	Substrate	Additive		Conv./%	Main products (yield, $\mu\text{mol } \%$)
		HCl/mmol	Water/mL		
1	Benzene	–	–	0	–
2	Benzene	1.0	0.5	0	–
3	Toluene	–	–	2.9	Benzaldehyde (2.9)
4	Toluene	1.0	0.5	3.8	Benzaldehyde (3.8)
5 ^b	Ethylbenzene	–	–	6.2	α -PEA (1.4), ACP (4.8)
6 ^b	Ethylbenzene	1.0	0.5	12.3	α -PEA (2.4), ACP (9.9)
7	Butanone	–	–	4.6	Acetic acid (2.7), butanedione (1.9)
8 ^c	Butanone	1.0	0.5	6.4	Acetic acid (3.8), butanedione (1.1)

^a Substrate (1.0 mmol), catalyst (0.014 mmol), acetonitrile (5.5 or 5.0 mL), O_2 (1 atm), temperature (36–38 °C), time (12 h), using 35 W of tungsten–bromine lamp as visible light source.

^b The calculated substrate conversion based on the main oxygenation products; α -PEA and ACP presented phenethylalcohol and acetophenone, respectively.

^c 3-Chloro-butanone (1.5% yield) was detected.

were irradiated by visible light for 12 h under O_2 , the characteristic absorbance of $W_{10}O_{32}^{4-}$ at $\lambda = 320$ nm was still well preserved in a pure MeCN (curve 5), in MeCN containing water (curve 6) or 10 M HCl and water (curve 8), with a concomitant slight increase in the absorbance at $\lambda = 265$ –270 nm. This indicates that the $W_{10}O_{32}^{4-}$ is relatively stable in these reaction media. However, the characteristic band at $\lambda = 320$ nm significantly decreased to become a shoulder in presence of only 10 M HCl, with a concomitant obvious increase in the absorbance at $\lambda = 255$ nm (curve 7), implying that the catalyst $W_{10}O_{32}^{4-}$ is unstable in this reaction medium and may be converted to some inactive species during its photo-catalysis oxygenation, as supported by the reaction results in Fig. 5.

Fig. 7 presents the cyclic voltammograms (CVs) of GCE for $W_{10}O_{32}^{4-}$ in various reaction media. Only a pair of quasi-reversible redox waves near $(-0.070 + (-0.329))/2 = -0.200$ V was observed for 5.0×10^{-3} M of $W_{10}O_{32}^{4-}$ in a pure CH_3CN (curve 1), which should be assigned to the redox process between W^{6+} and W^{5+} ions. Notably, the W^{6+}/W^{5+} redox waves of $W_{10}O_{32}^{4-}$ became strong and shifted to a more negative potential $((-0.265 + (-0.381))/2 = -0.323$ V) in the presence of water (curve 2), but to a more positive potential $((0.065 + (-0.101))/2 = -0.018$ V) in the presence of 10 M HCl (curve 3). In the co-existence of 10 M HCl and water, such a pair of redox waves appeared at $(-0.147 + (-0.305))/2 = -0.226$ V (curve 4). These findings indicate

that the oxidative capacity of catalyst in MeCN can be strengthened in the presence of 10 M HCl, but weakened in the existence of water. The peak to peak separation of the various CV curves followed an increasing sequence of curve 1 (0.259 V) > curve 3 (0.166 V) > curve 4 (0.158 V) > curve 2 (0.116 V), illustrating that the redox recycling between W^{6+} and W^{5+} ions in MeCN becomes easier with acidic aqueous solution than without it.

3.3. Photocatalytic mechanism

Based on the results presented here, as well as those in previous studies [46,47,51,60–66], it is apparent that the above data are better explained according to the following reaction pathway. Firstly, visible light illumination of the decatungstate ($W_{10}O_{32}^{4-}$) leads to the formation of a locally excited state [$W_{10}O_{32}^{4-*}$] that decays in less than 30 ps [62] to a relatively stable transient $W_{10}O_{32}^{4-*}$ with a lifetime of 65.5 ns [63–65] (Eq. (1)). It is most likely, this extremely reactive $W_{10}O_{32}^{4-*}$ with an oxyradical-like character [63,65] easily reacts with cyclohexane via a hydrogen atom abstraction or electron transfer mechanism [46,47,62–66]. In any case, the one electron reduced form of decatungstate ($HW_{10}O_{32}^{5-}$) is formed accompanying with a carbon centered radical intermediate (Cy^{\bullet} , Eq. (2)). Followed by addition of O_2 to the Cy^{\bullet} to form a cyclohexyl peroxy radical ($CyOO^{\bullet}$). The latter is likely converted to a cyclohexyl hydroperoxide ($CyOOH$) through the following pathway that the $HW_{10}O_{32}^{5-}$ is oxidized by the $CyOO^{\bullet}$ to its starting state $W_{10}O_{32}^{4-}$ via an electron transfer mechanism [51,53,61,65].

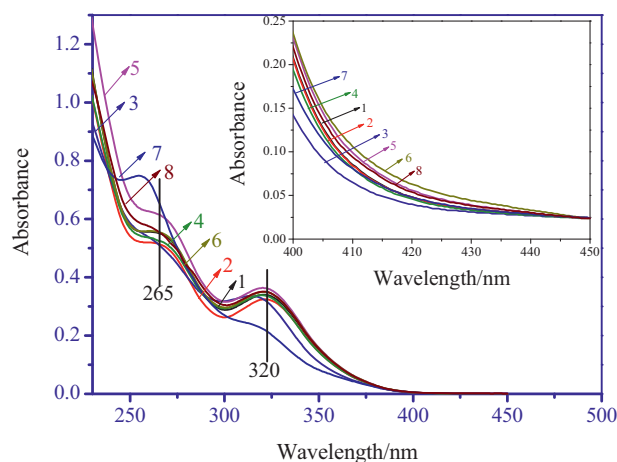


Fig. 6. The UV-vis spectra (200–500 nm) of $W_{10}O_{32}^{4-}$ (5.1×10^{-6} M) in MeCN solvent containing 1 mmol cyclohexane. (1) The system in a pure MeCN (5.5 mL); (2) the system in MeCN (5 mL) and H_2O (0.5 mL); (3) the system in MeCN (5.4 mL) and HCl (10 M, 0.1 mL); (4) the system in MeCN (4.9 mL), HCl (10 M, 0.1 mL) and H_2O (0.5 mL); (5) after using a visible light to irradiate the system 1 for 12 h; (6) after using a visible light to irradiate the system 2 for 12 h; (7) after using a visible light to irradiate the system 3 for 12 h; (8) after using a visible light to irradiate the system 4 for 12 h. Inset is the amplified absorption edge of $W_{10}O_{32}^{4-}$ (2.5×10^{-4} M) in a visible region.

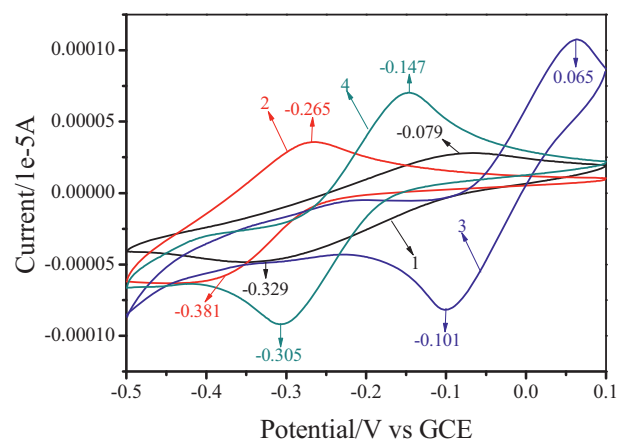
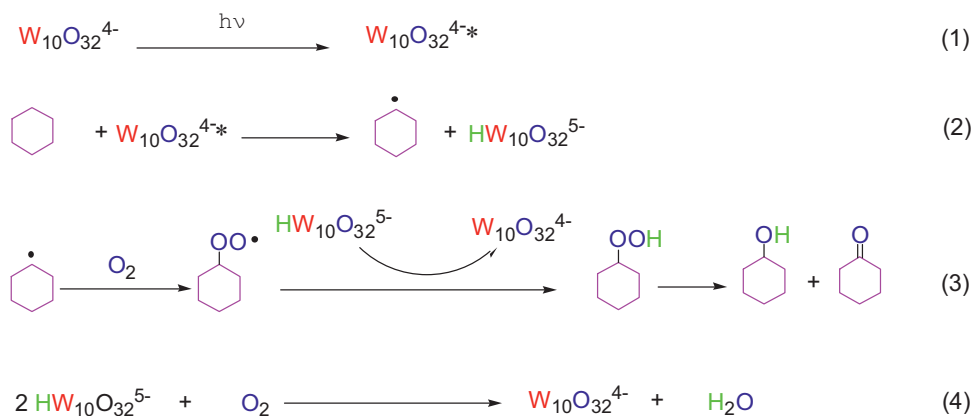


Fig. 7. Cyclic voltammograms (CVs) of $W_{10}O_{32}^{4-}$ (2.5×10^{-3} M) in MeCN with tetraethyl ammonium perchlorate (0.1 M). (1) A pure solvent MeCN (20 mL); (2) the mixed solvents H_2O (4.0 mL) and MeCN (16 mL); (3) the mixed solvents HCl (10 M, 0.4 mL) and MeCN (19.6 mL); (4) the mixed solvents H_2O (4.0 mL), HCl (10 M, 0.4 mL) and MeCN (15.6 mL).



Scheme 1. Photo-catalysis mechanism.

Finally, the CyOOH can be converted to form the corresponding alcohol and ketone. In addition, the $\text{HW}_{10}\text{O}_{32}^{5-}$ may be directly oxidized by molecular oxygen to the starting $\text{W}_{10}\text{O}_{32}^{4-}$ (Eq. (4)). Evidently, only using acidic additive is capable of improving the oxidative capacity of decatungstate, but obviously results in the decreased stability of decatungstate. The mediated effect of water on the decatungstate is just opposite with that mediated by the acidic additive. The co-mediated effect of water and acid may preserve a good stability and oxidative capacity of decatungstate and improve its redox recycling, which can lead an outstanding promotion effect on the visible light-driven photo-catalysis oxygenation (Scheme 1).

4. Conclusion

In summary, for the first time we have developed a visible light-triggered decatungstate to catalyze the selective oxidation of cyclohexane to cyclohexanol and cyclohexanone by molecular oxygen, and found that the photo-catalysis activity and cyclohexanone selectivity can be improved significantly in the presence of acidic aqueous solutions. Furthermore, this promoted effect commonly exists in the decatungstate-photocatalyzed oxygenation of other some organic compounds by molecular oxygen. It is anticipated that this photo-catalysis system will have competitive potential for the highly selective oxygenation of organic compounds with molecular oxygen to the corresponding oxygenated products under mild reaction conditions if its photo-catalysis efficiency is further improved.

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